Supporting Information for:
Concentrations, distribution and persistence of perfluoroalkylates
in sludge-applied soils near Decatur, Alabama, USA

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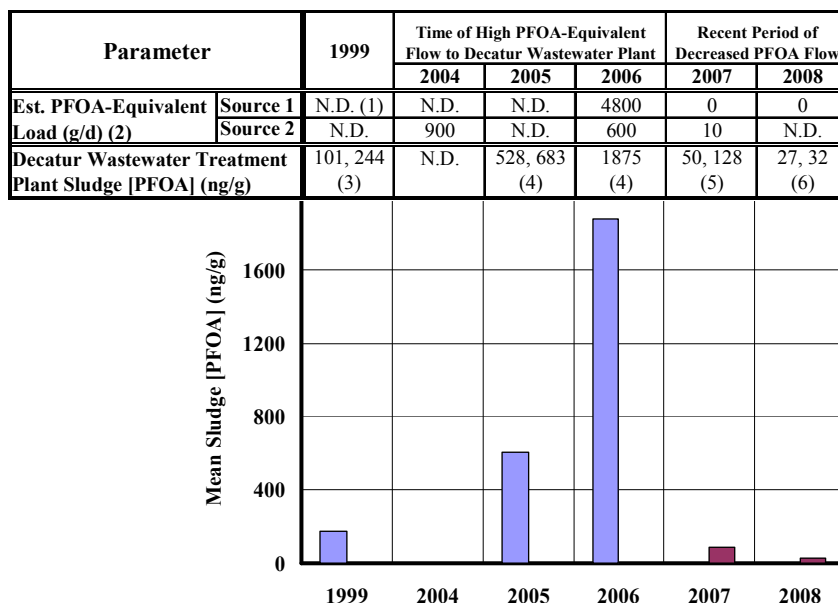
Derivation of Equation 3

Perfluorinated Compounds (PFCs) in Decatur Sludges

Because PFCs have not been regulated in sludges historically, records of PFC concentrations in Decatur sludges through time are fragmentary. Figure SI1 depicts the values of one PFC, perfluorooctanoic acid (PFOA), in Decatur sludges through time that have been documented in the public record along with estimated waste-stream loads to the Decatur facility for PFOA and chemical precursors to PFOA. This figure illustrates the precipitous drop in sludge [PFOA] concentrations that occurred between 2006 and 2007. This decrease was due to considerable reductions in the waste-stream load of PFOA and PFOA precursors from a number of industries discharging to the facility. Estimated loads for two of these industrial facilities are tabulated in Figure SI1 as well, and the sludge [PFOA] decrease between 2006 and 2007 coincides with the decrease in these loads.

The actual magnitude of the drop between 2006 and 2007 in sludge [PFOA] depicted in Figure SI1 is difficult to gauge because of differences in extraction and quantitation methodologies among the data. In particular, the 2007 data point is from Yoo et al. and is the result of an exhaustive effort to maximize the fraction of PFCs extracted from sludge [1]. This study showed that some commonly used extraction methodologies can yield substantially lower PFC concentrations, so the actual drop in sludge [PFOA] from 2006 to 2007 might be substantially greater than suggested by Figure SI1. Given this uncertainty, it is reasonable to estimate that Decatur sludge [PFOA] dropped one to two orders of magnitude between 2006 and 2007. Because of this large temporal variation in Decatur sludge [PFOA], and likely other [PFC]s as well, it is unreasonable to attempt a PFA mass balance of soil PFAs reported in this paper against PFA loadings calculated from sludge application rates.

For a qualitative perspective of the Decatur sludge [PFOA] values depicted in Figure SI1, Yoo et al. [1] reported [PFOA] = 8 to 20 ng/g for New York City sludge and ~30 ng/g for a standard reference sludge from the National Institute of Standards and Technology. In a study of Danish sludges, Bossi et al. [2] reported [PFOA] = 1 to 20 ng/g. Based on these data, the 2008 values for the Decatur sludge of 27 and 32 ng/g (Figure SI1) appear to be fairly typical of other sludges, but the 2006 and earlier values in Figure SI1 seem to be unusually high relative to other literature values for sludge [PFOA]. The timing of the initiation of elevated Decatur sludge [PFC]s is uncertain because of a paucity of data. Analytical results for 1999 record only slightly elevated levels of sludge PFOA at that time (Figure SI1). Overall, best estimates based on records submitted to EPA are that Decatur sludge [PFC]s increased in or about 2002. Based on this, Table SI1 tabulates the sludge applications to the sampled fields starting in 2002 as well as the time that elapsed between application of the last elevated-[PFOA] sludge (i.e., 2006) and the time of sampling.

Figure SI1. [PFOA] in Decatur Sludge and PFOA Loads in Selected Industrial Waste Sources to the Decatur Wastewater Treatment Plant through Time

Parameter		1999	Time of High PFOA-Equivalent Flow to Decatur Wastewater Plant			Recent Period of Decreased PFOA Flow	
			2004	2005	2006	2007	2008
Est. PFOA-Equivalent Load (g/d) (2)	Source 1	N.D. (1)	N.D.	N.D.	4800	0	0
	Source 2	N.D.	900	N.D.	600	10	N.D.
Decatur Wastewater Treatment Plant Sludge [PFOA] (ng/g)		101, 244 (3)	N.D.	528, 683 (4)	1875 (4)	50, 128 (5)	27, 32 (6)

(1) N.D. designates "not determined." (2) Estimated PFOA-Equivalent Loads were generated from records of waste-stream concentrations and flow rates submitted to regulatory agencies, by two of several fluoro-chemical-related industries contributing to the Decatur waste-stream, and not further identified to avoid entangling the science reported here with other possible issues. One Source reported in this figure reported concentrations of a PFOA precursor from which PFOA load was estimated as the stoichiometric equivalent. References for PFOA concentrations through time: 3) 3M Environmental Laboratory, 2001 [3]; 4) Weston Solutions, Inc., 2008 [4]; 5) Yoo et al., 2009; 6) ADEM, 2010. Because of the possible sensitivity of the data and estimates in this figure, we need to specify several limitations: i) these data are sufficiently fragmentary that no inference can be made other than PFOA, and likely other PFCs, were high for multiple years ending in 2006 and relatively lower from 2007 and forward in time -- neither the absence nor the presence of a trend prior to 2006 or after 2007 is intended to be implied by this figure; ii) there were other waste flows to the Decatur WWTP, whether these other streams constituted larger or smaller loads of PFCs than these reported estimates is left unevaluated by the authors of this paper; and iii) the summary depicted in this figure is for the research purposes of this paper only and is not part of any other effort in which the EPA may or may not be involved.

Table SI1: Fields, Sludge Applications & Soil Samples Collected

Survey Year & Field	Area (ha)	Sludge Applications Date	Dry Mass (metric tons) (1)	(tons/ha)	2007 Sampling Time since last app. (y)	ID	Depth (cm)	grab/ composite	2009 Sampling Time since last app. (y)	ID	Depth (cm)	grab/ composite
07A	10.9	2002	225	20.6								
		2003	92	29.1		3	0 to 10	grab				
		2004	0	29.1		3Dup	0 to 10	grab				
		2005	77	36.1		4	23 to 38	grab				
		2006	140	48.9	1.2	6	0 to 10	grab				
		2007	59									
		2008	175									
07B	3.2	2002	31	9.6						09B2-1	0 to 10	grab
		2003	75	32.7		7	0 to 10	grab		09B2-2	41 to 56	grab
&		2004	47	47.3		7Dup	0 to 10	grab		09B2-3	152 to 165	grab
		2005	51	63.1		9	0 to 10	grab		09B3-1	0 to 10	grab
09B		2006	12	66.7	1.2				2.7	09B3-2	41 to 56	grab
		2007	0							09B3-3	152 to 165	grab
		2008	16									
09C	2.8	2002	58	20.5								
		2003	47	37.1								
		2004	37	50.3						09C1-1	0 to 10	grab
		2005	24	58.7					3.7	09C1-2	36 to 51	grab
		2006	0							09C1-3	152 to 165	grab
		2007	0									
		2008	42									
09D	13.4	2002	21	1.6						09D1	0 to 10	composite
		2003	226	18.5						09D2	0 to 10	composite
		2004	71	23.8						09D3	0 to 10	composite
		2005	112	32.2						09D4	0 to 10	composite
		2006	79	38.0					2.7	09D5	0 to 10	composite
		2007	124							09D5Dup	0 to 10	composite
		2008	0									
09E	13.0	2002	0	0.0								
		2003	0	0.0						09E1	0 to 10	composite
		2004	0	0.0						09E2	0 to 10	composite
		2005	102	7.9						09E3	0 to 10	composite
		2006	180	21.8					2.7	09E4	0 to 10	composite
		2007	177							09E5	0 to 10	composite
		2008	179									
09F	14.6	2002	76	5.2						09F1	0 to 10	composite
		2003	173	17.1						09F1Dup	0 to 10	composite
		2004	279	36.3						09F2	0 to 10	composite
		2005	0	36.3						09F3	0 to 10	composite
		2006	71	41.1					2.7	09F4	0 to 10	composite
		2007	138							09F5	0 to 10	composite
		2008	97									
09G	8.1	2002	64	7.9								
		2003	69	16.4						09G1	0 to 10	composite
		2004	102	29.0					4.7	09G2	0 to 10	composite
		2005	0							09G3	0 to 10	composite
		2006	0							09G4	0 to 10	composite
		2007	0							09G5	0 to 10	composite
		2008	0									
09H										09H1	0 to 10	composite
Background Fields												
07Bgd	5.7					10	0 to 10	grab				
						11	0 to 10	grab				
09Bgd										09Bgd1-1	0 to 10	grab
										09Bgd1-2	38 to 53	grab
										09Bgd2-1	0 to 10	grab
										09Bgd2-2	38 to 53	grab

1) Sludge application rates reported to EPA in cubic yards. Reported here in dry metric tons using the conversion 1 yd^3 = 0.123 tons. "Metric tons" tabulates the tonnage applied to each field in the designated year. "Metric tons/ha" tabulates the cumulative sludge application for the designated field through 2006.

Chemicals. Except as noted below, all chemicals used in this study were of the highest purity offered by the suppliers, uniformly ≥97% purity. Perfluoro-n-hexanoic acid, perfluoro-n-octanoic acid, perfluoro-n-nonanoic acid, perfluoro-n-decanoic acid, perfluoro-n-[1,2-^{13}C]hexanoic acid, perfluoro-n-[1,2,3,4-^{13}C]octanoic acid, perfluoro-n-[1,2,3,4,5-^{13}C]nonanoic acid, perfluoro-n-[1,2-^{13}C]decanoic acid all were purchased as certified standards from Wellington Laboratories through TerraChem (Shawnee Mission, KS, USA). Formulae for these perfluorocarboxylic acids (PFCAs) and the acronyms used herein for these compounds, are summarized in Table SI2. Tetrabutylammonium hydrogen sulfate (TBAHS) and sodium carbonate, were purchased from Aldrich Chemical (Milwaukee, WI, USA). Acetonitrile (ACN), glacial acetic acid, methanol (MeOH) and methyl *tert*-butyl ether (MTBE) were purchased from Fisher Chemical (Fairlawn, NJ, USA). Oasis HLB solid-phase extraction (SPE) cartridges, 35-cm^3 capacity, were purchased from Waters (Milford, MA, USA).

Liquid Chromatograph, Tandem Mass-Spectrometer Analyses.

Acetonitrile/water extracts were analyzed on a Waters Acquity ultra-performance liquid chromatograph (UPLC) interfaced with a Waters Quattro Premier XE tandem mass spectrometer operated in negative electrospray-ionization mode. Typical mass chromatograms for the carboxylic acid and sulfonate analytes in an extract of sludge-applied surface soil are depicted in Figures SI1a and SI1b, respectively. As Figure SI1 depicts, some analytical peaks were complex. We integrated these peaks by setting software integration parameters so that integrations closely approximated the integration rules described in detail in Washington et al. [5]. All software-integrated peaks were checked and, if needed, adjusted manually according to these same integration rules. Efforts were made to reduce background noise in the system for PFOA by modifying the UPLC plumbing. Modifications included installation of polyaryletheretherketone (PEEK) tubing, removal of the degasser, installation of a C18 trap column (100mm × 2.1mm × 3.5µm) in the water eluent line immediately upgradient of the solvent mixer, and use of manually-degassed 18 MΩ water "polished" by passing through a Waters HLB solid phase extraction cartridge [6].

Each of the triplicate extractions of the 2007 survey was run on the LC/MS/MS three times. Each of the duplicate extractions of the 2009 survey was run four times.

In preparation for the 2009 sample analyses, it was discovered that the UPLC could not maintain a sufficiently stable eluent pressure. It was determined that the only way to achieve satisfactory pressure stability, within an acceptable sample-analysis timeframe, was to remove the trap column. With the trap column removed, the operating pressure range dropped to acceptable levels and stabilized the pressure variability. However, this altered the elution time windows for the analytes. Consequently, revised analytical and quantitation methods had to be developed for these samples (Tables 2 and 3). Because the extracts of this study were highly concentrated in analytes and other compounds, baseline was noisier than when we prepare the instrument for low-level detections and integration thresholds were set to accommodate this. Consequently, whatever small effect might have been imparted by removal of the trap column on blanks and samples was vanishingly small, well below detection limits.

All system operations were controlled by Waters MassLynx 4.1 and QuanLynx 4.1. Twenty microliters of extract were introduced to a Waters BEH C18 guard cartridge followed by a Waters BEH C18 analytical column, 100mm × 2.1mm × 2.1μm, maintained at 35 °C. The UPLC was operated using ACN and water eluents adjusted to pH 4 with glacial acetic acid. Pumping at a constant total flow of 0.5 mL/min, runs were started with 35% ACN, and then linearly ramped to 90% ACN over 5 min, held for 6 min, linearly ramped back to 35% ACN at 11.1 min, from which time the composition was held constant until the end of analysis at 13 min.

After UPLC elution, extracts were introduced to the mass spectrometer operated in ESI(-) mode with the capillary potential set at -600 V, the extractor potential at -2 V and the radio-frequency (RF) lens potential at 0.3 V (Table SI2). The source temperature was maintained at 140 °C. The N_2 generator desolvation gas was maintained at 350 °C and 800 L/h flow. The cone gas flow, also supplied by the N_2 generator, was set to 25 L/h. Analyte-specific instrumental parameters, including monitored transitions, were optimized for PFCs analysis. The low- and high-mass resolutions in the first quadrupole both were set to 13.0 (unitless ratio of direct to RF current voltages) and the ion energy was set to 0.7 eV. In the collision cell, the entrance was set to -3 V, the interior set to -16 V and the exit set to -1 V. The Ar collision gas was set to flow at 0.45 mL/m. Low- and high-mass resolutions in the third quadrupole both were set to 12.0 and the ion energy was set to 1.0 eV. The detector was operated in multiple-reaction-monitoring (MRM) mode, with the detector multiplier set to -700 V and the dwell time was set to 70 ms with the objective of achieving at least 15 scans per peak.

Chromatograms were smoothed using a second-order Savitsky-Golay algorithm and two five-point smoothes with a few exceptions to accommodate monitoring the high number of transitions in the method (Table SI3). Quantitation was performed using mass-labeled matrix internal standards. Quantitation for C6, C8, C9, C10, C11, and C12, analytes was accomplished using isotopic dilution since isotopically labeled standards were available. C7 and PFOS were quantitated using the mass-labeled C8 ($^{13}C_4$-PFOA) and C10 ($^{13}C_2$-PFDA) matrix internal standards, respectively. Calibrations were constructed with linear regressions of untransformed data, and plots of peak area/internal standard area versus calibration standard concentration/ internal standard area; 1/X weighting was applied for regression. Standards injected on the instrument ranged from 0.9 to 4800 pg/g. The lowest standard concentrations that were used to generate the calibration curves were those levels for which the calibration lines maintained a central tendency for repeated measures of the standards. Final calibration curves consisted of 11-14 standard concentrations of the targeted species spanning from 5 to 4800 pg/g. Standards were interspersed with sample extracts and blanks throughout the sample-analysis runs. The limit of quantification (LOQ) was designated as the value of the lowest standard for which average standard readings included in the calibration are within ± 30% (Table SI3) of the prepared standard value, or tighter constraints as determined by the analyst; see Table SI3 for analyte-specific LOQ criterion. Sample extracts were diluted as needed to get their concentrations to fall within the instrument calibration

range using 60:40 ACN:H$_2$O spiked with appropriate concentrations of all matrix internal standards.

Table SI2: Analytes, and Liquid Chromatograph & Mass spectrometer Parameters for Analyses

Compound	Nominal Retention Time (RT)				Number of Transitions	Number of Transitions Per Function	Parent Anion Mass (m/z)	Cone Potential (V)	Quan Ion Mass (m/z)	Quan Ion Collision Energy (eV)	Primary Qual Ion Mass (m/z)	Primary Qual Ion Collision Energy (eV)	2nd Qual Ion Mass (m/z)	2nd Qual Ion Collision Energy (eV)
	Apex RT (min)	Front RT (min)	Tail RT (min)	Delta T from Prev. Apex (min)										
Function 1 Time Interval 0 to 1.1 Min														
Perfluoroprionoic acid (C3)	0.65	0.4	0.9		2	5	162.80	14	118.80	11	69.80	25		
Perfluorobutanoic acid (C4; PFBA)	0.70	0.4	1.0	0.05	1		212.85	13	168.80	10	Irregular response			
^{13}**C$_4$-Perfluorobutanoic acid ((M+4)C4; MPFBA)**	0.70	0.4	1.0	0.05	1		216.90	14	171.80	10	Irregular response			
Perfluoropentanoic acid (C5; PFPA)	0.95	0.6	1.3	0.25	1		262.80	13	218.85	10	Irregular response			
Function 2 Time Interval 0.9 to 2.1 Min														
Perfluorohexanoic acid (C6; PFHxA)	1.35	1.0	1.7	**0.40**	2	7	312.80	13	268.85	10	118.80	20		
^{13}**C$_2$-Perfluorohexanoic acid ((M+2)C6; MPFHxA)**	1.35	1.0	1.7	**0.40**	1		314.80	14	269.85	10	*119.30*	*20*		
Perfluorobutane sulfonate (S4; PFBS)	1.50	1.2	1.8	0.15	2		298.90	40	79.85	30	98.85	40		
Perfluoroheptanoic acid (C7; PFHpA)	1.80	1.5	2.1	0.30	2		362.70	13	318.80	10	168.85	18		
Function 3 Time Interval 1.8 to 3.2 Min														
Perfluorooctanoic acid (C8; PFOA)	2.30	1.9	2.7	**0.50**	2	11	412.70	14	368.75	10	168.85	18		
^{13}**C$_4$-Perfluorooctanoic acid ((M+4)C8; M4PFOA)**	2.30	1.9	2.7	**0.50**	1		416.70	14	371.70	10	*171.85*	*18*		
^{13}**C$_8$-Perfluorooctanoic acid ((M+8)C8; M8PFOA)**	2.30	1.9	2.7	**0.50**	1		420.70	13	375.70	11	*171.85*	*20*		
Perfluorohexane sulfonate (S6; PFHxS)	2.50	2.1	2.9	0.20	2		398.90	50	79.85	40	98.85	40		
Perfluorononanoic acid (C9; PFNA)	2.75	2.4	3.1	0.15	2		462.70	15	418.70	11	218.85	18		
13C5-Perfluorononanoic acid ((M+5)C9; MPFNA)	2.75	2.4	3.1	0.15	1		467.70	15	422.70	12	*222.90*	*18*	*218.90*	*18*
Function 4 Time Interval 2.4 to 3.4 Min														
Perfluoroheptane sulfonate (S7; PFHpS)	2.95	2.6	3.3	0.20	2	2	448.90	50	79.90	40	98.90	40		
Function 5 Time Interval 2.9 to 4.4 Min														
Perfluorodecanoic acid (C10; PFDA)	3.35	3.0	3.7	**0.40**	2	11	512.90	15	468.70	11	218.85	20		
^{13}**C$_2$-Perfluorodecanoic acid ((M+2)C10; MPFDA)**	3.35	3.0	3.7	**0.40**	1		514.90	15	470.00	12				
Perfluorooctane sulfonate (S8; PFOS)	3.55	3.2	3.9	0.20	2		498.90	60	79.85	50	98.85	40		
8:2 Fluorotelomer unsaturated acid (8:2FTUCA; U8:2)	3.65	3.3	4.0	0.10	2		456.70	16	392.70	18	*342.70*	*40*		
^{13}**C$_2$-8:2 Fluorotelomer unsaturated acid ((M+2)8:2FTUCA)**	3.65	3.3	4.0	0.00	1		458.70	16	393.70	16	*343.70*	*40*		
Perfluoroundecanoic acid (C11; PFUA)	3.90	3.6	4.2	0.25	2		562.70	15	518.70	12	218.85	20		
^{13}**C$_2$-Perfluoroundecanoic acid ((M+2)C11; MPFUA)**	3.90	3.6	4.2	0.25	1		564.90	15	520.00	13				
Function 6 Time Interval 4.0 to 15.0 Min														
Perfluorododecanoic acid (C12; PFDoA)	4.50	4.2	4.8	**0.60**	2	10	612.70	16	568.70	13	318.70	20		
^{13}**C$_2$-Perfluorodecanoic acid ((M+2)C12; MPFDoA)**	4.50	4.2	4.8	**0.60**	1		614.90	16	570.00	13				
10:2 Fluorotelomer unsaturated acid (10:2FTUCA; U10:2)	4.65	4.4	4.9	0.15	2		557.00	16	493.00	17	*443.00*	*38*		
^{13}**C$_2$-10:2 Fluorotelomer unsaturated acid ((M+2)10:2FTUCA)**	4.65	4.4	4.9	0.15	1		559.00	16	494.00	17				
Perfluorotridecanoic acid (C13; PFTrA)	5.15	4.9	5.4	0.50	2		662.75	16	618.70	13	318.70	22		
Perfluorotetradecanoic acid (C14; PFTeA)	5.80	5.5	6.1	0.65	2		712.75	18	668.70	14	318.70	24		

Table SI3: Integration & Optimization Parameters for Analyses

Compound	Savitzky Golay Smoothing # Points; # Smooths	Quan. Qual. Ratio & Tolerance (%)	Standards Range (pg/g) (# Levels)	Internal Standard	1/x-Weighted Calibration Equation	Correlation Coefficient (r^2)	Limit of Quantitation (pg/g)	Limit of Quantitation (LOQ) Definition
Function 1 Time Interval 0 to 1.1 Min								
Perfluoroprionoic acid (C3)	5; 2							
Perfluorobutanoic acid (C4; PFBA)	5; 2							
^{13}C$_4$-Perfluorobutanoic acid ((M+4)C4; MPFBA)	5; 2							
Perfluoropentanoic acid (C5; PFPA)	0; 0							
Function 2 Time Interval 0.9 to 2.1 Min								
Perfluorohexanoic acid (C6; PFHxA)	5; 2	21. +/- 44%	0.9 - 4800 (14)	(M+2)C6	0.011*[pg/g] + 0.018	0.997	18	≥LOQ within 20% tolerance
^{13}C$_2$-Perfluorohexanoic acid ((M+2)C6; MPFHxA)	5; 2		Invariant		Matrix Internal Standard			
Perfluorobutane sulfonate (S4; PFBS)	5; 2	4.8 +/- 44%	9 - 4800 (12)	(M+2)C6	0.005*[pg/g] + 0.016	0.997	18	≥LOQ within 20% tolerance
Perfluoroheptanoic acid (C7; PFHpA)	0; 0	3.1 +/- 44%	5 - 4800 (13)	(M+4)C8	0.011*[pg/g] + 0.006	0.995	18	≥LOQ within 20% tolerance
Function 3 Time Interval 1.8 to 3.2 Min								
Perfluorooctanoic acid (C8; PFOA)	5; 2	3.31 +/- 44%	0.9 - 4800 (14)	(M+4)C8	0.013*[pg/g] + 0.002	0.994	18	≥LOQ within 20% tolerance
^{13}C$_4$-Perfluorooctanoic acid ((M+4)C8; M4PFOA)	5; 2		Invariant		Matrix Internal Standard			
^{13}C$_8$-Perfluorooctanoic acid ((M+8)C8; M8PFOA)	5; 2		0.9 - 4800 (14)	(M+4)C8	0.013*[pg/g] + 0.002	0.997	5	LOQ within 30% tolerance, >LOQ within 20%
Perfluorohexane sulfonate (S6; PFHxS)	5; 2	2.0 +/- 44%	5 - 4800 (13)	(M+4)C8	0.008*[pg/g] - 0.012	0.992	38	LOQ within 30% tolerance, >LOQ within 20%
Perfluorononanoic acid (C9; PFNA)	5; 2	4.3 +/- 44%	0.9 - 4800 (14)	(M+5)C9	0.011*[pg/g] + 0.015	0.996	18	≥LOQ within 20% tolerance
13C5-Perfluorononanoic acid ((M+5)C9; MPFNA)	5; 2		Invariant		Matrix Internal Standard			
Function 4 Time Interval 2.4 to 3.4 Min								
Perfluoroheptane sulfonate (S7; PFHpS)	5; 2	1.5 +/- 44%	5 - 4800 (13)	(M+5)C9	0.003*[pg/g] + 0.002	0.973	56	≥LOQ within 30% tolerance
Function 5 Time Interval 2.9 to 4.4 Min								
Perfluorodecanoic acid (C10; PFDA)	5; 2	6.8 +/- 44%	5 - 4800 (13)	(M+2)C10	0.011*[pg/g] + 0.016	0.992	18	≥LOQ within 20% tolerance
^{13}C$_2$-Perfluorodecanoic acid ((M+2)C10; MPFDA)	5; 2		Invariant		Matrix Internal Standard			
Perfluorooctane sulfonate (S8; PFOS)	5; 2	1.32 +/- 44%	5 - 4800 (12)	(M+2)C10	0.004*[pg/g] + 0.003	0.990	38	≥LOQ within 20% tolerance
8:2 Fluorotelomer unsaturated acid (8:2FTUCA; U8:2)	5; 2		5 - 4800 (13)	(M+2)8:2FTUCA	0.010*[pg/g] + 0.005	0.992	18	≥LOQ within 20% tolerance
^{13}C$_2$-8:2 Fluorotelomer unsaturated acid ((M+2)8:2FTUCA)	5; 2		Invariant		Matrix Internal Standard			
Perfluoroundecanoic acid (C11; PFUA)	5; 2	8.8 +/- 44%	5 - 4800 (13)	(M+2)C11	-2.66e-7*[pg/g]^2 + 0.010*[pg/g] - 0.010	0.997	18	≥LOQ within 20% tolerance
^{13}C$_2$-Perfluoroundecanoic acid ((M+2)C11; MPFUA)	5; 2		Invariant		Matrix Internal Standard			
Function 6 Time Interval 4.0 to 15.0 Min	5; 2							
Perfluorododecanoic acid (C12; PFDoA)	5; 2	10.8 +/- 44%	0.9 - 4800 (14)	(M+2)C12	-7.54e-7*[pg/g]^2 + 0.010*[pg/g] + 0.006	0.998	38	≥LOQ within 20% tolerance
^{13}C$_2$-Perfluorodecanoic acid ((M+2)C12; MPFDoA)	5; 2		Invariant		Matrix Internal Standard			
10:2 Fluorotelomer unsaturated acid (10:2FTUCA; U10:2)	5; 2		0.9 - 4800 (14)	(M+2)10:2FTUCA	0.010*[pg/g] + 0.006	0.991	18	≥LOQ within 20% tolerance
^{13}C$_2$-10:2 Fluorotelomer unsaturated acid ((M+2)10:2FTUCA)	5; 2		Invariant		Matrix Internal Standard			
Perfluorotridecanoic acid (C13; PFTrA)	5; 2	12.9 +/- 44%	5 - 4800 (13)	(M+2)C12	-8.86e-7*[pg/g]^2 + 0.013*[pg/g] + 0.033	0.997	18	≥LOQ within 20% tolerance
Perfluorotetradecanoic acid (C14; PFTeA)	5; 2	16.9 +/- 44%	5 - 4800 (13)	(M+2)C12	-9.72e-7*[pg/g]^2 + 0.013*[pg/g] + 0.002	0.996	18	≥LOQ within 20% tolerance
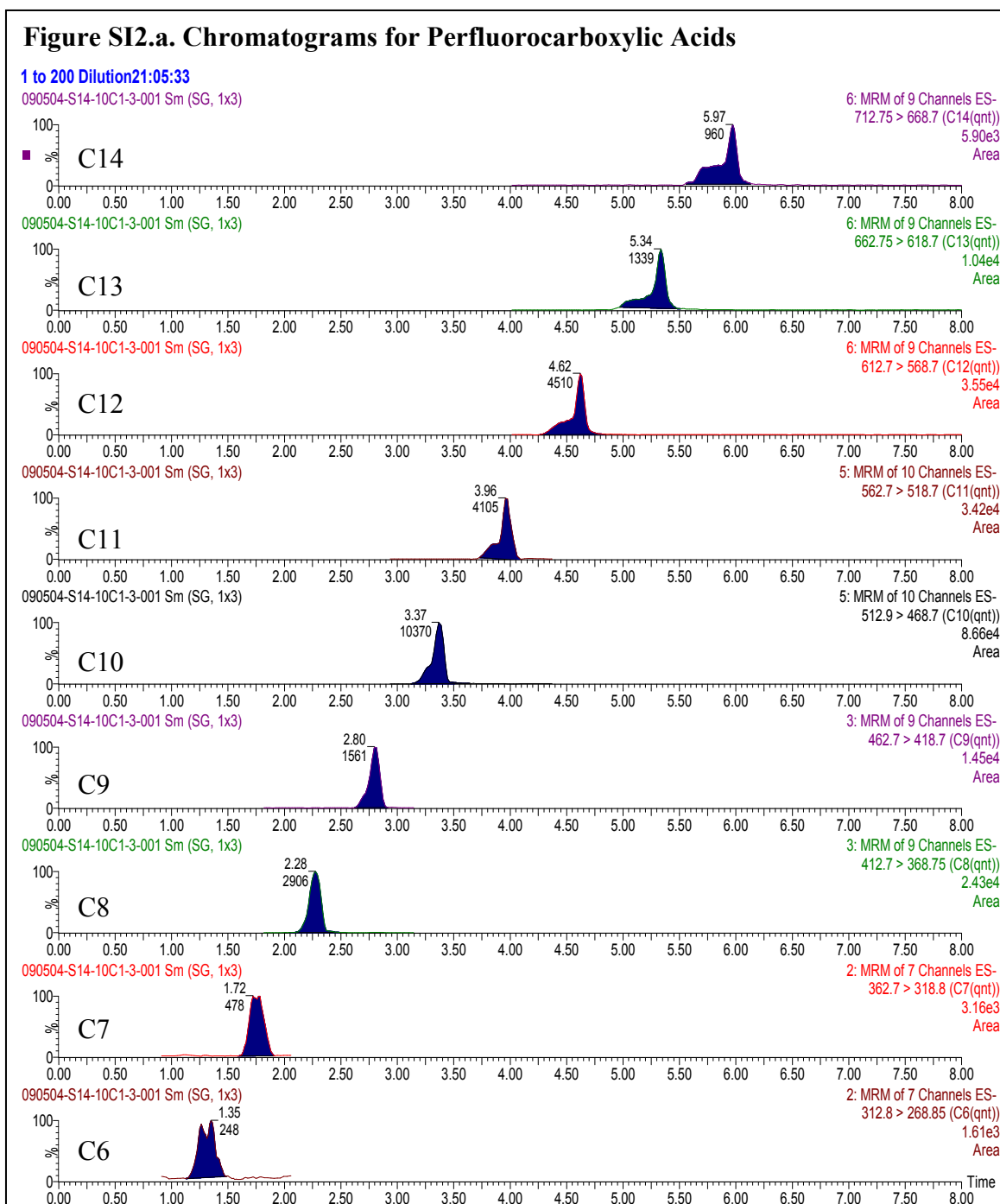
Figure SI2.a. Mass chromatogram of perfluorocarboxylic acids for an extract of a sludge-applied surface soil, sample 09B3-1. Given the complex matrix imparted by the surface soil-sludge mixture, analyte peaks commonly were complex even after cleanup, possibly reflecting the presence of isomers [7] or complexation with soil-solution cations. No attempt was made to separate isomers. Integration rules for each analyte were established after review of many sample runs.

Figure SI2.b. Chromatograms for Perfluorosulfonates and Unsaturated Acids

10:2 FTUCA – Not detected

PFOS

8:2 FTUCA – Not detected

PFHpS < LOQ

PFHxS < LOQ

PFBS < LOQ

Figure SI2.b. Mass chromatogram of unsaturated acids and perfluorosulfanates for an extract of a sludge-applied surface soil, sample 09B3-1. Given the complex matrix imparted by the surface soil-sludge mixture, analyte peaks commonly were complex even after cleanup, possibly reflecting the presence of isomers [7] or complexation with soil-solution cations. No attempt was made to separate isomers. Integration rules for each analyte were established after review of many sample runs.

Data-Quality Metrics
The following tables (Table SI4 through SI8 and SI10) report data that reflect the quality of the data in this study. The significance of each of these metrics is summarized below.

Method Blanks. No PFAs were detected in method blanks.

Standard Curve Back-Prediction. The data we report herein were acquired in three analytical runs, 2007 survey, 2009 surface soils and 2009 subsurface soils. Table SI4 summarizes typical mean back-calculated values for the calibration-curve standards for each PFC. For all analytical runs, the mean back-calculated values for all standards above the LOQ generally fell within the quality criterion of ± 30% of the calculated value.

Blank and Reference-Soil Samples Taken to the Fields. Table SI5 documents the expected low to non-detect PFC analyte levels for the QC sand and Cowart soil samples. For the sand blanks, analyte values all were less than the LOQ values (Table SI5).
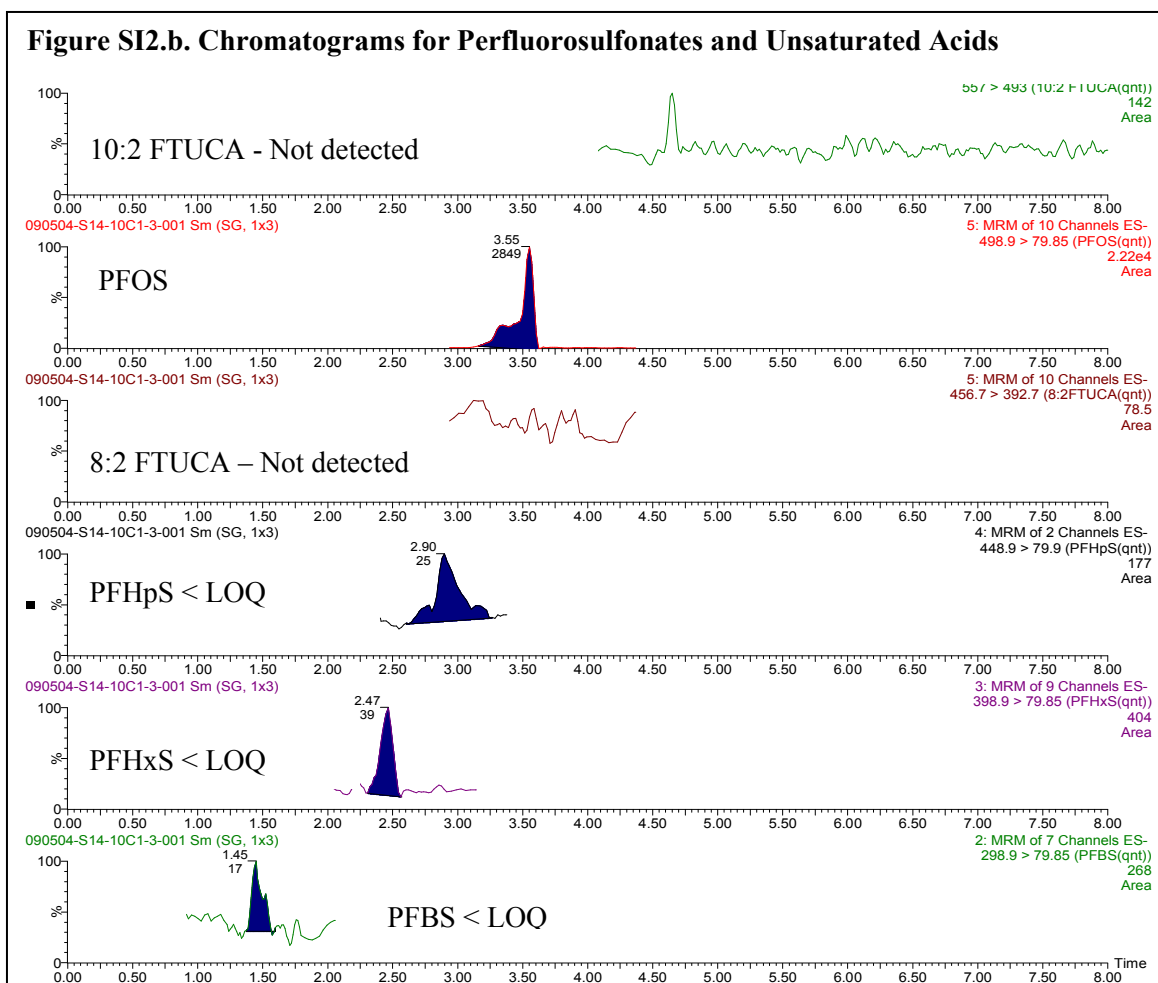
Background Fields. Table SI6 documents the expected low to non-detect PFC analyte levels for the background field samples on both the 2007 and the 2009 surveys. Most background sample analytes fell below the LOQs and the few detected analytes fell just above the LOQ. The two subsurface samples had several detects. In particular, 09Bgd2-2 had moderate levels of several analytes including PFOA and PFOS; however, these values still are one or more orders of magnitude lower than those of the subsurface samples drawn from the sludge-applied fields.

Field Duplicates. Table SI7 summarizes the field-duplicate sample PFC results and associated percent relative difference (%RD) for the 2009 survey. Field-duplicate sample results for the targeted acid species and PFOS suggest reasonably good reproducibility for samples collected separately from the same location in the field, with most analytes falling within 50% of each other.

Standard Addition. The average recovery for the added concentration of PFC standards to the soil samples (Table SI8) was within the acceptable range of ±30% of calculated values for all analytes.

Recovery Internal Standards. We do not report recovery values for the 2007 survey data; because of unexpectedly high levels we encountered for the acids when we analyzed the extracts, we had to dilute the extracts drastically enough to get them to fall within the calibration range that the recovery internal standard level was diluted below the LOQ. With the 2007 survey for experience, we accommodated the high acids concentrations and the recoveries generally fell very close to 100%, all samples falling between 59-112% (Table SI10).

Table SI4: Percent Deviation of Mean Back-Predicted Values for Perfluorinated Chemical Standard Curve Points for Subsurface Soils Analytical Run [1]

Std Value pg/g	C6	C7	C8	C9	C10	C11	C12	C13	C14	S4	S6	S7	S8	U8:2	U10:2	M8C8
0.913	**108.1**	ND	ND	**53.3**	**42.4**	**151.9**	2.2	28.7	9.5	ND	ND	20.5	ND	**97.2**	16.8	**130.0**
4.502	8.3	12.2	9.4	-22.3	**-34.5**	**-54.8**	-12.6	**-31.7**	2.2	20.5	29.4	9.4	-25.6	7.7	13.3	-2.3
9.224	-6.2	17.9	0.6	6.2	-28.4	-25.2	-5.1	-4.3	-6.5	3.3	-8.9	-4.9	-20.0	**45.8**	7.3	-24.4
18.13	-6.9	7.8	6.2	-5.5	7.6	2.9	-1.1	-1.3	-4.6	-2.1	6.7	**-37.8**	13.3	-11.6	-9.1	1.2
38.07	4.8	1.3	-9.7	-19.9	13.9	-0.6	-4.1	-1.0	-0.4	-6.4	2.0	-1.9	9.7	-27.0	-2.9	-14.9
55.72	11.0	-5.9	-4.7	-1.4	6.5	2.3	5.4	6.4	7.4	5.6	-5.5	8.0	20.3	-27.7	1.3	-8.3
72.94	4.4	-2.1	-1.7	2.2	8.6	-2.9	3.9	-2.2	-10.8	-4.4	-1.5	16.8	0.3	13.0	-0.7	-12.2
93.02	-2.4	-4.6	4.8	-5.5	-0.8	9.5	6.2	2.1	2.0	-7.9	-5.3	-10.7	3.5	11.9	4.1	-5.7
231.5	-5.1	-6.3	-0.1	14.5	-7.1	2.2	2.4	0.8	2.1	-3.0	-1.3	16.3	0.9	-28.5	1.7	-7.4
483.9	-1.1	-9.2	-4.5	-1.6	3.0	-2.7	2.0	3.8	1.6	-4.7	-5.1	-0.1	-4.0	-16.4	11.7	-9.8
721	-3.1	-5.0	-1.8	-0.3	4.4	2.5	0.8	1.0	-6.2	-6.8	-9.7	-20.1	4.1	-23.8	4.0	-9.7
986.3	2.0	-7.0	0.8	-0.4	8.3	5.1	-0.3	-2.1	1.1	3.1	-5.2	7.2	24.4	-17.2	-7.3	-7.2
2380	1.6	-5.4	0.5	2.4	-4.8	4.2	-2.9	-1.8	2.8	0.0	-0.1	9.5	7.2	-20.7	7.6	-4.7
4763	-0.6	6.2	12.8	-1.3	-3.1	-3.5	3.3	3.7	-7.7	0.9	6.1	-4.2	-9.5	20.3	-4.5	7.2

[1] Bold values do not meet the quality criterion of being within 30% of the nominal standard concentration. Where present, the emboldened values fall below the limit of quantitation.

Table SI5: Analytical Results (pg/g dry soil) for QC Samples Taken to the Field (1)

QC Sample	C6 (pg/g soil)	C7 (pg/g soil)	C8 (pg/g soil)	C9 (pg/g soil)	C10 (pg/g soil)	C11 (pg/g soil)	C12 (pg/g soil)	C13 (pg/g soil)	C14 (pg/g soil)	S4 (pg/g soil)	S6 (pg/g soil)	S7 (pg/g soil)	S8 (pg/g soil)	U8:2 (pg/g soil)	U10:2 (pg/g soil)
2007 Survey Sand blank	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
2009 Survey Sand blank	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
QC Soil	147	105	363	114	153	114	110	41	23	55	71	<LOQ	1532	<LOQ	<LOQ

(1) The QC soil is the 'Cowart soil,' a commercial potting soil that we keep in stock. It is high in organic matter (8.7% dry-weight basis) and heterogeneous, but very low, PFA concentrations relative to the soils of this study, and has non-detectable levels of FTOHs. LOQs reported here are normalized to sand or soil mass using the nominal masses called for in the extraction method.

Table SI6: Summary of Background Field Soils

QC Sample	Sample Depth (cm)	Statistic	C6 (pg/g soil)	C7 (pg/g soil)	C8 (pg/g soil)	C9 (pg/g soil)	C10 (pg/g soil)	C11 (pg/g soil)	C12 (pg/g soil)	C13 (pg/g soil)	C14 (pg/g soil)	S4 (pg/g soil)	S6 (pg/g soil)	S7 (pg/g soil)	S8 (pg/g soil)	U8:2 (pg/g soil)	U10:2 (pg/g soil)	M8C8 (% Rec.)
2007 Survey																		
07Bgd-10	0--10		<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	
07Bgd-11	0--10		<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	
2009 Survey																		
09Bgd1-1	0--10	Mean	<LOQ	0.03	0.17	0.08	0.05	0.04	<LOQ	<LOQ	<LOQ	0.09	<LOQ	<LOQ	1.9	<LOQ	<LOQ	71
		Stan. Dev.		0.01	0.02	0.03	0.01	0.05				0.03			0.3			33
09Bgd1-2	38--53	Mean	117	<LOQ	64	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	83
		Stan. Dev.	27		6													1
09Bgd2-1	0--10	Mean	0.02	0.04	0.21	0.05	<LOQ	0.03	<LOQ	<LOQ	<LOQ	0.06	<LOQ	<LOQ	1.25	<LOQ	<LOQ	89
		Stan. Dev.	0.02	0	0.03	0.01		0				0.03			0.01			1
09Bgd2-2	38--53	Mean	243	110	226	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	248	<LOQ	<LOQ	79
		Stan. Dev.	9	15	6										32			6

Table SI7: Summary of Duplicate Field Samples (ng/g dry soil)

Sample ID	C6	C7	C8	C9	C10	C11	C12	C13	C14	S4	S6	S7	S8	U8:2	U10:2
09F1	19	38	190	91	684	199	396	65	70	<LOQ	<LOQ	<LOQ	127	<LOQ	<LOQ
09F1Dup	27	53	269	132	986	233	526	81	114	<LOQ	<LOQ	<LOQ	189	<LOQ	<LOQ
Rel % Diff	35	35	34	37	36	16	28	21	48	NA	NA	NA	39	NA	NA
09D5	<LOQ	30	153	76	509	133	245	40	52	<LOQ	<LOQ	<LOQ	177	<LOQ	<LOQ
09D5Dup	<LOQ	49	264	110	683	171	349	61	90	<LOQ	<LOQ	<LOQ	245	<LOQ	<LOQ
Rel % Diff	NA	47	53	37	29	25	35	41	53	NA	NA	NA	32	NA	NA

Table SI8. Standard Addition of 100 pg of Perfluorinated Chemicals to Selected Field Sample Extracts

Sample ID	pg C6	pg C7	pg C8	pg M8C8	pg C9	pg C10	pg C11	pg C12	pg C13	pg C14	pg S4	pg S6	pg S7	pg S8	pg U8:2	pg U10:2
LCMSMS Analyzed Added Mass of Analyte																
09C1-1SA	111	104	106	104	78	113	95	111	135	136	113	100	124	167	109	116
09C1-2SA	118	116	106	105	118	135	107	103	116	124	119	109	142	119	114	112
09C1-3SA	117	99	111	107	96	107	98	115	116	114	115	109	111	98	107	131
09B2-1SA	115	115	127	109	93	124	84	90	109	115	103	121	119	116	109	93
09B3-1SA	107	131	146	116	101	167	65	115	142	130	131	109	127	189	118	109
Actual Added Mass of Analyte																
09C1-1SA	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104	104
09C1-2SA	107	107	107	107	107	107	107	107	106	106	106	106	106	106	106	106
09C1-3SA	109	109	109	109	109	109	109	109	108	108	108	108	108	108	108	108
09B2-1SA	107	107	107	107	107	107	107	107	107	107	107	107	107	107	107	107
09B3-1SA	107	107	107	107	107	107	107	107	107	107	107	107	107	107	107	107

|	C6	C7	C8	M8C8	C9	C10	C11	C12	C13	C14	S4	S6	S7	S8	U8:2	U10:2
Percent Recovery of Added Analyte via LCMSMS Analysis																
09C1-1SA	107	100	102	100	75	108	92	106	130	131	109	96	119	161	105	112
09C1-2SA	111	109	99	99	111	127	100	97	109	116	111	102	134	112	107	105
09C1-3SA	108	91	102	99	88	99	90	106	107	105	106	100	102	90	98	120
09B2-1SA	107	107	118	102	87	116	79	84	102	108	96	113	112	109	102	88
09B3-1SA	100	122	136	108	95	156	61	108	133	121	122	102	119	177	111	102
Avg % Rec'y	107	106	112	102	91	121	84	100	116	116	109	103	117	130	105	105
SD % Rec'y	4.0	11.6	15.8	4.0	13.0	21.9	15.1	9.9	14.4	10.5	9.4	6.3	11.6	37.2	4.6	12.2

Table SI9: Summary of Sludge-Applied Soils Sampled in 2007 (ng/g dry soil; values are for 3 repeated measures of each of 3 extractions)

| Field ID	Sample ID	Depth (cm)	Summary Statistic	C3 (ng/g)	C4 (ng/g)	C5 (ng/g)	C6 (ng/g)	C7 (ng/g)	C8 (ng/g)	C9 (ng/g)	C10 (ng/g)	C11 (ng/g)	C12 (ng/g)	C13 (ng/g)	C14 (ng/g)	S4 (ng/g)	S6 (ng/g)	S7 (ng/g)	S8 (ng/g)	U6:2 (ng/g)	U8:2 (ng/g)	U10:2 (ng/g)
07A	3	0--10	Mean	<870	<420	143	328	425	2531	649	2029	481	491	<100	<100	<100	<100	<100	1296	<100	<100	<100
			Stan. Dev.			7.3	16.3	21.7	67.0	78.8	94.8	81.1	71.7						117.2			
07A	3Dup	0--10	Mean	<870	<420	<100	199	314	1895	464	1593	425	743	140	209	<100	<100	<100	1409	<100	<100	<100
			Stan. Dev.				7.5	48.2	278.8	25.5	50.0	39.1	21.4	5.5	16.3				249.6			
07A	6	0--10	Mean	<870	<420	<100	<100	139	818	221	760	219	328	<100	112	<100	<100	<100	715	<100	<100	<100
			Stan. Dev.					14.8	86.2	22.4	109.5	25.0	22.2		13.5				182.9			
07B	7	0--10	Mean	<870	<420	<100	111	239	1340	428	1496	370	445	100	<100	<100	<100	<100	979	<100	<100	<100
			Stan. Dev.				13.4	12.4	102.8	61.8	191.3	30.6	13.5	6.5					173.9			
07B	7Dup	0--10	Mean	<870	<420	<100	<100	154	541	125	398	100	140	<100	<100	<100	<100	<100	276	<100	<100	<100
			Stan. Dev.					7.1	38.4	6.4	23.4	22.8	10.0						69.9			
07B	9	0--10	Mean	<870	<420	<100	131	273	1598	484	2088	687	1240	245	345	<100	<100	<100	972	<100	<100	<100
			Stan. Dev.				10.1	54.2	296.6	70.6	111.9	123.7	224.6	30.7	39.2				318.4			

Table SI10: Summary of Sludge-Applied Soils Sampled in 2009 (ng/g dry soil; values are for 4 repeated measures of each of 2 extractions)

| Field ID	Sample ID	Depth (cm)	Summary Statistic	C6 (ng/g)	C7 (ng/g)	C8 (ng/g)	C9 (ng/g)	C10 (ng/g)	C11 (ng/g)	C12 (ng/g)	C13 (ng/g)	C14 (ng/g)	S4 (ng/g)	S6 (ng/g)	S7 (ng/g)	S8 (ng/g)	U8:2 (ng/g)	U10:2 (ng/g)	M8C8 (%Rec.)
09D	1	0–10	Mean	35	80	312	118	528	126	179	27	32	<6.65	<14.1	<20.1	203	<6.65	<6.65	98
			Stan. Dev.	4.9	11.7	37.0	14.2	110.1	28.7	2.0	1.5	5.5				53.7			6.6
09D	2	0–10	Mean	12	42	233	115	562	146	206	34	47	<6.65	<14.1	<20.1	164	<6.65	<6.65	82
			Stan. Dev.	17.0	1.2	6.5	2.0	18.4	14.9	14.3	0.0	5.6				17.0			16
09D	3	0–10	Mean	20	39	183	90	566	154	304	54	79	<6.65	<14.1	<20.1	202	<6.65	<6.65	81
			Stan. Dev.	2.9	5.0	21.1	1.7	46.5	5.1	48.7	9.8	13.4				27.0			9.0
09D	4	0–10	Mean	24	51	255	137	830	311	498	75	135	<6.65	<14.1	<20.1	325	<6.65	<6.65	99
			Stan. Dev.	1.3	1.5	19.7	6.7	12.3	13.5	3.1	17.6	1.6				25.9			20
09D	5	0–10	Mean	<6.65	30	153	76	509	133	245	40	52	<6.65	<14.1	<20.1	177	<6.65	<6.65	76
			Stan. Dev.		1.4	17.0	1.5	43.4	2.0	10.0	3.3	27.1				6.1			5.3
09D	5Dup	0–10	Mean	11	49	264	110	683	171	349	61	90	<6.65	<14.1	<20.1	245	<6.65	<6.65	105
			Stan. Dev.	14.9	0.6	19.4	25.1	9.0	29.7	12.0	12.3					14.7			26
09E	1	0–10	Mean	<6.65	16	105	34	132	21	30	<6.65	<14.1	<6.65	<14.1	<20.1	35	<6.65	<6.65	102
			Stan. Dev.		2.2	20.3	4.6	19.1	0.9	0.9						5.5			15
09E	2	0–10	Mean	<6.65	11	64	26	141	26	35	<6.65	<14.1	<6.65	<14.1	<20.1	31	<6.65	<6.65	110
			Stan. Dev.		1.7	14.2	2.8	8.6	0.5	1.0						0.1			35
09E	3	0–10	Mean	<6.65	13	87	47	231	29	34	<6.65	<14.1	<6.65	<14.1	<20.1	36	<6.65	<6.65	87
			Stan. Dev.		1.0	1.3	0.2	1.8	0.7	5.4						3.7			25
09E	4	0–10	Mean	17	31	185	67	343	44	71	10	19	<6.65	<14.1	<20.1	82	<6.65	<6.65	87
			Stan. Dev.	3.0	6.2	33.3	9.6	24.6	5.0	3.5	3.2	1.0				33.8			26
09E	5	0–10	Mean	19	41	236	93	445	62	92	12	21	<6.65	<14.1	<20.1	82	<6.65	<6.65	80
			Stan. Dev.	0.1	1.9	31.2	5.4	25.7	7.5	1.3	0.3	0.2				4.3			4.3
09F	1	0–10	Mean	19	38	190	91	684	199	396	65	70	<6.65	<14.1	<20.1	127	<6.65	<6.65	99
			Stan. Dev.	0.1	1.5	9.3	10.6	87.2	15.6	51.5	2.6	5.0				5.3			0
09F	1Dup	0–10	Mean	27	53	269	132	986	233	526	81	114	<6.65	<14.1	<20.1	189	<6.65	<6.65	85
			Stan. Dev.	0.3	3.6	13.3	12.3	94.1	5.5	11.9	1.6	1.2				19.0			12
09F	2	0–10	Mean	<6.65	21	120	67	420	138	240	41	51	<6.65	<14.1	<20.1	81	<6.65	<6.65	84
			Stan. Dev.		3.1	5.0	6.8	21.0	1.7	20.7	7.7	2.7				3.3			0.04
09F	3	0–10	Mean	26	50	249	104	614	146	257	40	36	<6.65	<14.1	<20.1	122	<6.65	<6.65	97
			Stan. Dev.	3.0	5.8	31.0	4.0	2.7	3.3	13.4	1.8	23.1				6.9			25
09F	4	0–10	Mean	<6.65	19	87	49	323	104	174	33	19	<6.65	<14.1	<20.1	58	<6.65	<6.65	79
			Stan. Dev.		1.9	3.8	1.1	5.2	2.3	1.3	3.6	19.5				0.5			9.1
09F	5	0–10	Mean	16	28	139	73	405	108	239	38	63	<6.65	<14.1	<20.1	73	<6.65	<6.65	69
			Stan. Dev.	4.0	2.0	23.7	12.0	70.0	9.1	17.9	0.8	1.6				15.2			29
09C	1-1	0–10	Mean	<6.65	14	84	83	419	126	186	36	34	<6.65	<14.1	<20.1	203	<6.65	<6.65	68
			Stan. Dev.		4.1	23.4	12.3	57.0	15.7	2.7	3.8	1.6				1.5			26
09C	1-2	36–51	Mean	0.91	2.14	21.90	8.18	5.01	0.49	0.46	<0.14	0.14	<0.09	<0.13	<0.23	7.37	<0.09	<0.15	86
			Stan. Dev.	0.11	0.16	1.82	0.58	0.16	0.02	0.02		0.02				0.56			9
09C	1-3	152–165	Mean	2.51	5.02	13.57	1.03	2.05	0.61	1.05	0.20	0.31	<0.09	<0.13	<0.23	1.78	<0.09	<0.15	86
			Stan. Dev.	0.51	0.92	1.84	0.05	0.20	0.04	0.06	0.04	0.04				0.05			16
09B	2-1	0–10	Mean	<6.65	11	60	39	349	171	341	66	65	<6.65	<14.1	<20.1	149	<6.65	<6.65	111
			Stan. Dev.		0.86	0.26	2.9	30.3	6.66	10.4	6.64	3.5				0.93			5.3
09B	2-2	41–56	Mean	1.15	3.20	79.62	36.15	24.06	3.06	1.61	0.27	0.25	<0.09	0.23	0.26	20.99	<0.09	<0.15	93
			Stan. Dev.	0.31	0.30	6.30	2.05	1.84	0.23	0.10	0.03	0.05		0.06	0.04	2.26			6
09B	2-3	152–165	Mean	1.42	5.25	9.81	0.25	0.55	0.21	0.52	0.29	0.90	<0.09	0.15	<0.23	0.60	<0.09	<0.15	79
			Stan. Dev.	0.14	0.27	0.43	0.03	0.04	0.04	0.09	0.04	0.13		0.04		0.12			3
09B	3-1	0–10	Mean	28	61	317	129	670	279	293	68	49	<6.65	<14.1	<20.1	408	<6.65	<6.65	110
			Stan. Dev.	3.7	0.22	9.29	6.81	42.3	12.7	19.4	9.4	4.9				48.9			18
09B	3-2	41–56	Mean	4.29	6.24	15.69	2.59	5.07	0.50	0.41	<0.14	<0.09	<0.09	0.16	<0.23	3.39	<0.09	<0.15	76
			Stan. Dev.	0.38	0.55	2.11	0.36	0.39	0.04	0.02				0.02		0.17			12
09B	3-3	152–165	Mean	2	2	3	0	0	<0.17	<0.11	<0.14	<0.09	<0.09	<0.13	<0.23	0	<0.09	<0.15	89
			Stan. Dev.	0.3	0.4	0.6	0.0	0.0								0.1			12
09G	1	0–10	Mean	<6.65	17	94	58	353	139	215	37	49	<6.65	<14.1	<20.1	118	<6.65	<6.65	86
			Stan. Dev.		5.8	10.4	3.3	7.1	8.6	5.6	1.7	3.6				8.3			1.6
09G	2	0–10	Mean	12	21	133	95	557	238	407	70	82	<6.65	<14.1	<20.1	160	<6.65	<6.65	112
			Stan. Dev.	1.7	1.3	4.9	11.7	79.2	23.9	15.5	1.4	0.9				2.8			0.94
09G	3	0–10	Mean	<6.65	14	119	82	277	101	158	25	26	<6.65	<14.1	<20.1	88	<6.65	<6.65	109
			Stan. Dev.		1.6	3.8	1.9	33.9	1.3	13.8	2.2	14.5				3.7			16
09G	4	0–10	Mean	<6.65	16	123	89	414	142	261	46	76	<6.65	<14.1	<20.1	99	<6.65	<6.65	86
			Stan. Dev.		2.3	2.6	0.8	14.8	12.9	13.5	3.4	11.2				6.6			4.6
09G	5	0–10	Mean	<6.65	7	54	34	163	58	92	16	24	<6.65	<14.1	<20.1	61	<6.65	<6.65	59
			Stan. Dev.		0.1	7.6	2.3	14.2	7.2	1.1	0.7	3.6				4.7			0.12
09H	1	0–10	Mean	<0.018	<0.018	0.17	0.06	0.12	0.07	<0.038	<0.018	<0.018	<0.018	<0.038	<0.056	4.5	<0.018	<0.018	102
			Stan. Dev.			0.02	0.00	0.01	0.00							0.3			9
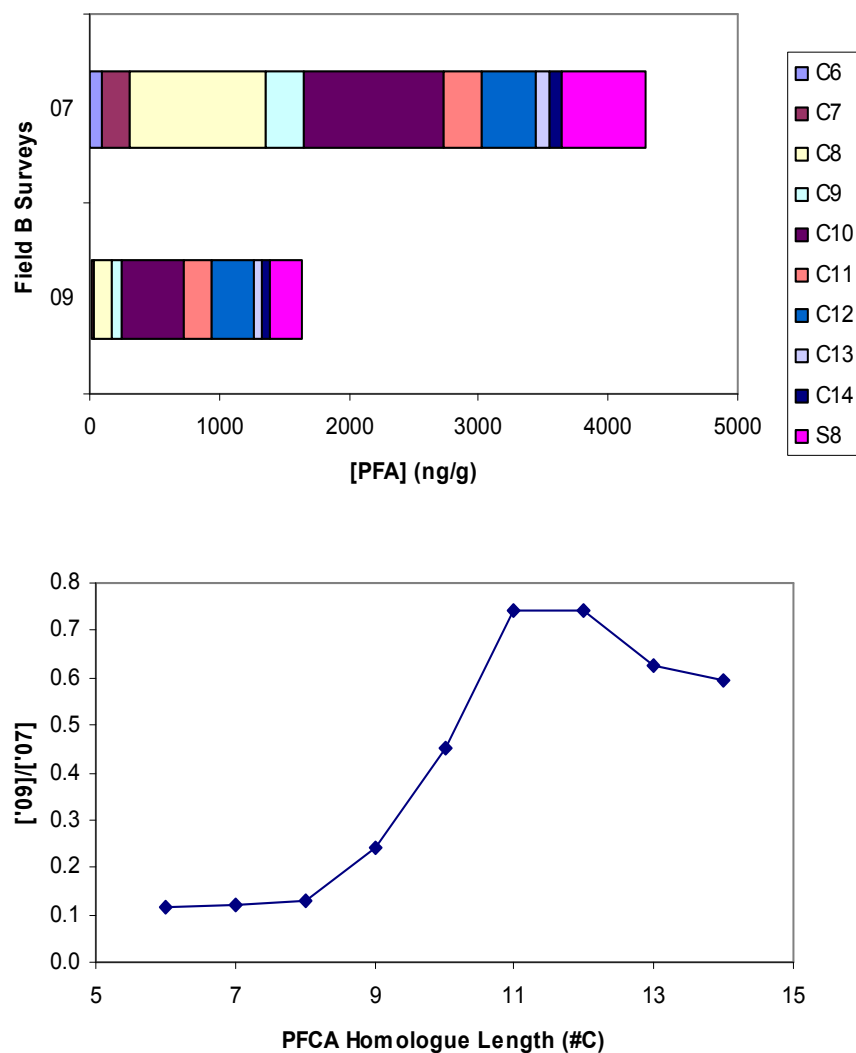
Figure SI3: Field B '07 vs '09 Survey. A) Geometric-mean surface-soil PFA concentrations (ng/g dry soil) in field B, representing 07B (n=3, samples 7 & 7Dup both included) and 09B (n=2); B) Ratio of measured geometric-mean [PFCA] (2009/2007) vs homologue length; evidently longer chains generally were retained more than shorter chains.
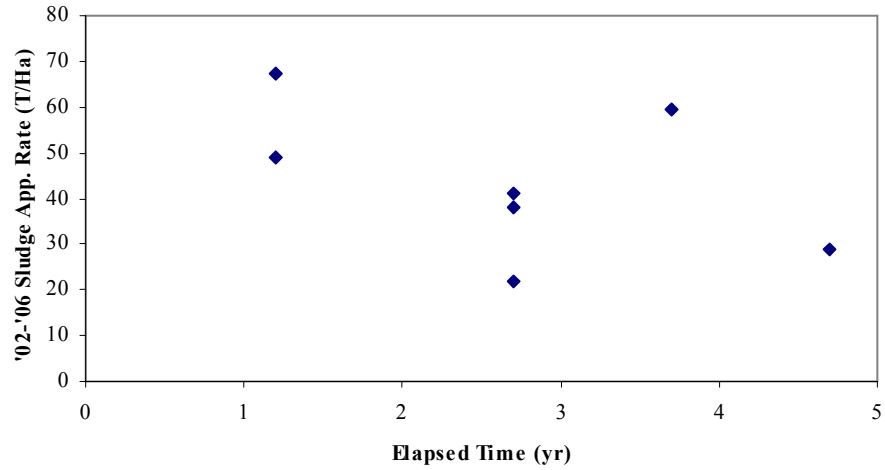
Figure SI4: Plot for the period when Decatur [PFA]s were particularly highly concentrated, 2002-2006 (Figure SI1), in variable space of 'sludge application rate (T/Ha)' vs 'time between last sludge application and sample collection (yr)' using data summarized in Table SI1. Sludge application rate is not significantly correlated (p=0.05) with time since sludge application. Consequently, the effect of sludge application rate and time since last application can be evaluated as separate independent variables for their possible effect on soil [PFA]s.
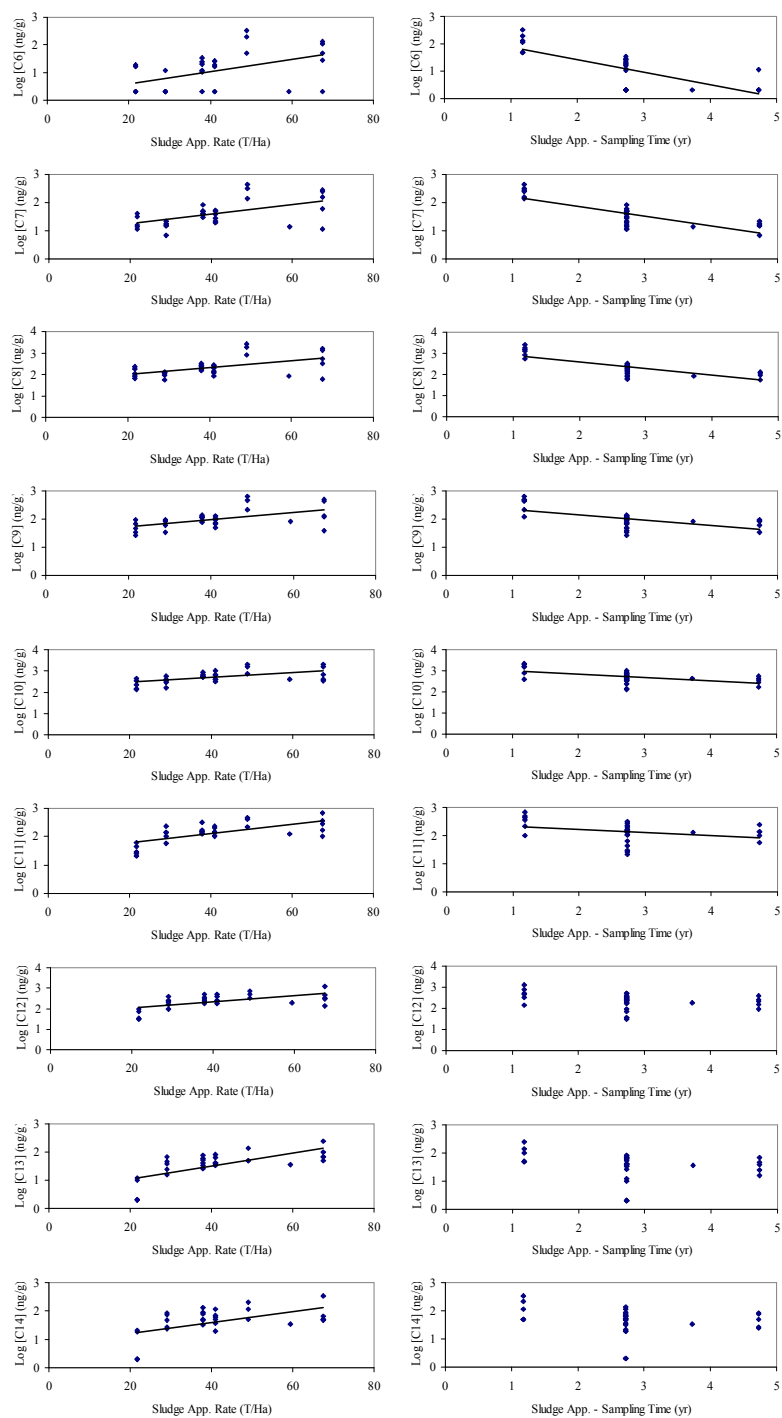
Figure SI5: Log [PFA]s (ng/g dry soil; n=31) in surface soils vs. sludge application rate and vs. interval between last sludge application and soil sampling for the period of high Decatur sludge[PFC]s, 2002-2006. Trend lines are shown for significantly correlated variables (Table 1). Note that the F statistics (Table 1) for: 1) short chains are higher for time as an independent variable than sludge-application rate; and 2) long chains are higher for sludge-application rate than time. See text for discussion.
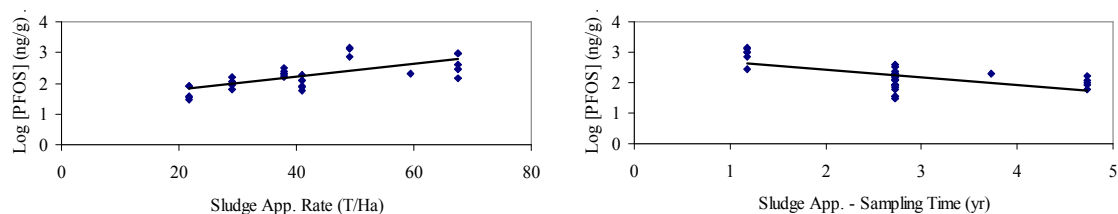
Figure SI6: Log [PFOS] (ng/g dry soil; n=31) in surface soils vs. sludge application rate and vs. interval between last sludge application and soil sampling for the period of high Decatur sludge[PFC]s, 2002-2006. Trend lines are shown for significantly correlated variables (Table 1). See text for discussion.
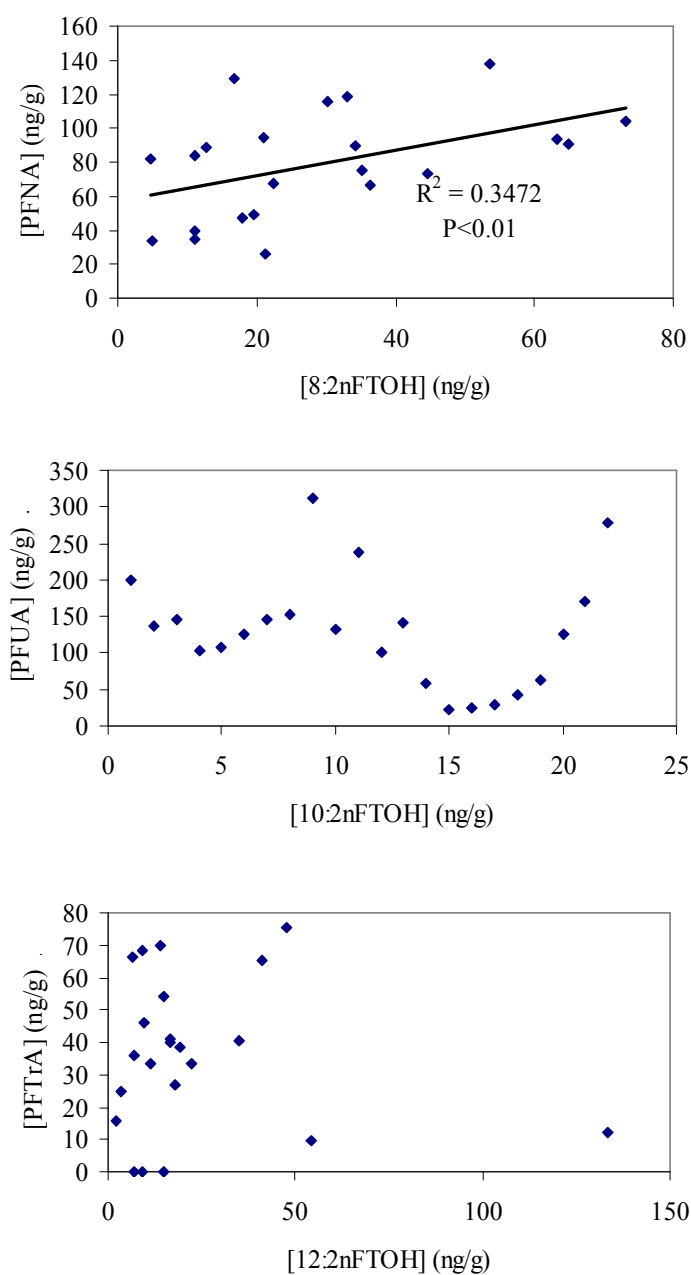
Figure SI7: Odd-numbered PFCAs (n=23) in surface-soil samples as a function of their possible *n*-FTOH precursors (ng/g dry soil). A minor biological reaction pathway has been shown to proceed via ∀ oxidation to form odd-numbered acids from *n*-FTOHs [8]. For the three plots above, only 8:2*n*FTOH → PFNA exhibits a significant relationship for our data.

Derivation of Equation 3

When the PFOA precursor 7:2sFTOH is present in sludge that is applied to soil, the change in PFOA soil concentration ([PFOA]) over time is mediated by in-growth from 7:2sFTOH according to its first-order degradation constant ($k^d_{7:2sFTOH}$) and loss of PFOA by any of several processes, e.g., leaching, plant uptake, degradation, according to a net first-order loss constant (k_{PFOA}):

$$\frac{d[PFOA]}{dt} = k^d_{7:2sFTOH}[7:2sFTOH] - k_{PFOA}[PFOA] \qquad (SI1)$$

Upon integration, Equation SI1 yields:

$$\Delta t = t - 0 = t = \frac{\ln\{k^d_{7:2sFTOH}[7:2sFTOH] - k_{PFOA}[PFOA]\}}{-k_{PFOA}} + C \qquad (SI2)$$

Where C is an integration constant. Solving for [PFOA]:

$$[PFOA] = \frac{k_{7:2sFTOH}[7:2sFTOH] - e^{k_{PFOA}(C-t)}}{k_{PFOA}} \qquad (SI3)$$

Designating the initial [PFOA] at time=0 as [PFOA]$_0$:

$$[PFOA]_0 = \frac{k_{7:2sFTOH}[7:2sFTOH] - e^{k_{PFOA}C}}{k_{PFOA}} \qquad (SI4)$$

Solving for C:

$$C = \frac{\ln\{k_{7:2sFTOH}[7:2sFTOH] - k_{PFOA}[PFOA]_0\}}{k_{PFOA}} \qquad (SI5)$$

Substituting Equation SI5 into SI2 and solving for [PFOA]:

$$[PFOA] = \frac{k_{7:2sFTOH}[7:2sFTOH](1 - e^{-k_{PFOA}t})}{k_{PFOA}} + [PFOA]_0 e^{-k_{PFOA}t} \qquad (SI6)$$

Supporting Information References

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